triplet for all CH_2N protons). In an outside complexation, the spectrum would display a lack of symmetry under the coalescence temperature of the exchange (30 °C).

In summary, the ionic character of the solution, the large value for K_s (which can be attributed to the "cryptate effect"), and the symmetry of the spectrum under the coalescence temperature strongly suggest that $[2.2.2]–I^+$ is an inside complex. A more detailed discussion will appear in a full paper.

Jean-Louis Pierre,* Henri Handel, Pierre Labbé
Raymond Le Goaller

*Laboratoire de Chimie Organique
Université Scientifique et Médicale de Grenoble
B.P. 53X-38041 Grenoble-Cedex, France*

Received March 17, 1980

Metal–Metal Distances in a Platinum Acetamide Blue

Sir:

We report here the determination of some Pt–Pt distances in a platinum acetamide blue (PAB) from a Fourier analysis of its X-ray diffraction pattern. Platinum blues have elicited much interest recently not only because of their reported antitumor activity[1,2] but also because of their intense color which stands out against the paleness of most mononuclear platinum compounds. This intense color has been postulated to arise from the presence of Pt–Pt bonds and chains. Therefore, it is of particular importance to ascertain the presence or absence of a strong Pt–Pt interaction. However, it appears that the overwhelming majority of blues isolated so far are amorphous or very difficult to crystallize, and for this reason their structures have, with few exceptions, eluded direct determination. To date, we are aware of only two studies that have given significant structural information on blues: first, the crystal and molecular structure determination of *cis*-diammineplatinum α-pyridone blue[4] (α-PB) which established that this blue is composed of tetranuclear platinum chains, and second, an extended X-ray absorption fine structure study[5] of two uridine blues in which it was concluded that platinum atoms ~2.9 Å apart are present in these blues.

The PAB was prepared by the method of Hofmann and Bugge.[6] The products obtained from this synthesis vary from batch to batch.[3] The particular PAB sample used in this study has been described previously.[3] It was chosen because it exhibits the interesting average oxidation state of 3+ for platinum as determined by ceric ion titration, it is paramagnetic, and it has an average molecular weight of only 372 in water despite the intense blue (ϵ = 3560 cm^{-1} L/mol of Pt at 6740 Å) of the solution.

The X-ray data were obtained with a General Electric powder diffractometer by using a copper target tube and an argon flow proportional counter with a pulse height selector. The balanced filter technique (nickel and cobalt filters) was used so that the resulting diffraction data are essentially due to the copper $K\alpha$ lines alone (λ = 1.542 Å). The sample consisted of a paste of 131 mg of PAB and 24 mg of mineral oil formed into a rectangular slab 3 cm × 1 cm. For measurements with 2θ less than 20°, a 0.5° entrance slit was used while a 3° slit was used for angles greater than 20°. The quantity 2θ is defined as the angle between the incident and diffracted beams. A 1° receiving slit was used

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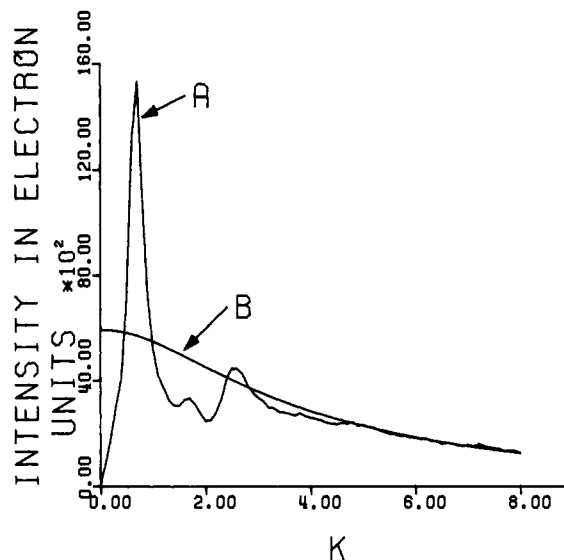

Figure 1. Scattering curves for PAB. Curve A is the normalized experimental intensity curve corrected for polarization and Compton scattering. Curve B is the total calculated independent scattering calculated from tabulated values of the atomic scattering factors [*Int. Tables X-Ray Crystallogr.*, 99 (1974)].
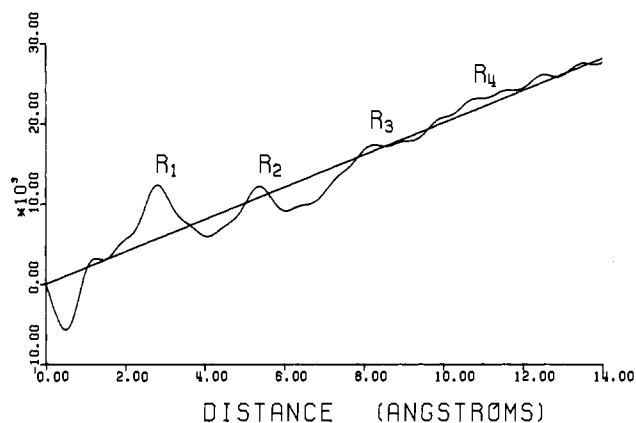

Figure 2. Pair function distribution curve of platinum acetamide blue. Only peaks due to platinum–platinum pairs will be expected to appear because the scattering power of X-rays is so much greater for platinum than for the other atoms of this compound.

throughout. Data were recorded for k = 0.3–8.0 at intervals of 0.1 (k = $4\pi \sin \theta/\lambda$). After correction for air scattering and polarization, the intensity curve was normalized and the Compton scattering subtracted.[8a,b] For this purpose the sample composition was taken to be Pt, 1; O, 3.61; N, 1.99; C, 7.51; H, 14.94, based on the elemental analysis of the PAB, and the mineral oil was assumed to have the formula CH_2.

The corrected scattering curves for our sample and the pair function distribution derived[8a] from it are shown in Figures 1 and 2, respectively. The very negative peak below 1 Å in the distribution curve is due in part to the fact that points were not collected for k > 8. Otherwise, the distribution curve shows prominent maxima at 2.76 (R_1), 5.36 (R_2), 8.02 (R_3), and 10.58 (R_4) Å.[9] The first distance is assigned to the Pt–Pt bond length in the PAB sample. It compares well with the average Pt–Pt separation in the metal (2.775 Å[10] with bond number 0.5). It is also comparable to the Pt–Pt separation in catenated partial oxidation complexes such as α-PB (2.78, 2.88 Å; $Pt^{2.25}–Pt^{2.25}$ tetranuclear chain)[4] and $K_2Pt(CN)_4Br_{0.3}\cdot 2.3H_2O$ (2.887 Å;

(8) (a) The relations used to derive the radial distribution are from B. E. Warren, "X-Ray Diffraction", Addison-Wesley, Reading, MA, 1969, Chapter 10. (b) Compton scattering factors were obtained from D. T. Cramer and J. B. Mann, *J. Chem. Phys.*, **47**, 1892 (1969).

(9) Error bars for these numbers have not been evaluated as there is no simple or direct way of accomplishing this.

$Pt^{2.2}$–Pt one-dimensional chain).[11] However, it is much longer than the 2.466 Å reported for the Pt(III)–Pt(III) bond length in $K_2[Pt_2(SO_4)_4(H_2O)_2]$,[12] a binuclear complex, not a chain complex. It is also appreciably longer than the expected length of a covalent Pt–Pt single bond as found in $Pt_2(C_5H_5)_2(C_5H_5C_5H_4)$ [$Pt^{(I)}$–$Pt^{(I)}$ 2.58 Å],[13] $Pt_2S[P(C_6H_5)_3]_3$ [$Pt^{(I)}$–$Pt^{(I)}$ 2.65 Å],[14] and [Pt_3-$(CO)_3(\mu\text{-}CO)_3]_n^{2-}$, n = 2, 3, or 5 [$Pt^{(0)}$–$Pt^{(0)}$ 2.66 Å].[15]

The above comparisons lend support to the formulation of PAB as a partial oxidation platinum chain complex. This is reinforced by the fact that R_2, R_3, and R_4 are approximate multiples of R_1 (R_2/R_1 = ~1.92-4, R_3/R_1 = ~2.91-3, R_4/R_1 = ~3.83-4), suggesting the presence in PAB of entities consisting of at least four or five rather linearly bound platinum atoms. On the basis of R_1 and R_2, the angle between adjacent Pt–Pt bonds is 152°. This is significantly smaller than in α-PB (164°). With the assumption of a planar zigzag chain of five platinum atoms with an angle of 152° between adjacent bonds, and a bond length of 2.76 Å, the Pt–Pt distances in the chain are 2.76, 5.36, 8.07, and 10.72 Å. These are in reasonable agreement with the observed distances in view of the simple planar geometry assumed.

Peaks in the pair function distribution curve associated with Pt–Pt intermolecular distances are expected to be considerably broader in general than those associated with intramolecular distances because the latter should exhibit a more discrete series of values in the amorphous PAB. The nearest neighbor distance is the most likely to assume a narrow enough range of values so as to yield an observable peak. Here, this distance will be essentially equal to the chain diameter. The width of chains similar to those in α-PB, with bridging acetamido ligands, is about 10 Å. This distance can be accommodated by R_4. However, as seen above, R_4 fits well the estimated length of a pentanuclear platinum chain in PAB, and it is therefore more appropriately assigned only to the latter, although the assignment is not without some uncertainty.

It is of interest, from a practical point of view, to find out if it is possible to correlate in a simple, yet reasonably accurate, way a Pt–Pt distance with a maximum in the scattering curve. With the assumption that the scattering results solely from platinum atoms displaced by a distance d from one another, a simple relation for the scattering intensity is given by[16] eq 1 with $k = 4\pi \sin\theta/\lambda$.

$$I_{eu} \propto \frac{\sin(kd)}{kd} \qquad (1)$$

The function $\sin(kd)/kd$ has the form of a strongly damped sine wave, with a maximum at $kd = 7.728$. Therefore, I_{eu} has a maximum at the scattering angle θ_{max} given by eq 2. Now, if

$$\theta_{max} = \sin^{-1}\left(\frac{7.728\lambda}{4\pi d}\right) \qquad (2)$$

$d = 2.76$ Å and $\lambda = 1.54$ Å, $\theta_{max} = 20°$ from eq 2. A strong maximum is indeed observed on the experimental scattering curve for PAB in the region, namely, at 18°. Application of eq 2 in reverse results in the calculated Pt–Pt distance corresponding to $\theta_{max} = 18°$ being $d = 3.07$ Å. Although this number deviates appreciably (+0.31 Å) from the one given by the radial distribution, it is low enough to suggest significant Pt–Pt interaction. However, it indicates that eq 2 is not accurate enough for quantitative work in this type of system.[17]

In conclusion, this preliminary X-ray diffraction study of a platinum acetamide blue reveals the presence of platinum chains

involving at least four or five metal atoms and a Pt–Pt bond length of 2.76 Å. The presence of platinum chains is consistent with the spectroscopic properties of PAB, and it is similar in this respect to α-PB. It is likely that PAB consists of a mixture of oligomers, with tetranuclear or pentanuclear chains accounting for a high enough proportion of the sample to be observable. Further information such as the proportion of each kind of chain can, in principle, be extracted from the scattering curve. However, our present data are not sufficiently extensive and precise to allow this in a reliable way. We hope to present a more detailed and complete study in the future. We feel it to be of interest to carry out X-ray studies of other blues, including other PAB samples, to determine the range of Pt–Pt bond distances and chain nuclearity in blues, and to correlate these with the spectroscopic and antitumor properties of blues.

M. P. Laurent, J. Biscoe, H. H. Patterson*

Departments of Chemistry and Physics
University of Maine, Orono, Maine 04469

Received June 2, 1980

Interception of the Cope Chairlike Transition-State Product during the Tandem Cope–Claisen Rearrangement: A Route to an Ambrosanolide Synthon

Sir:

The preference for a chairlike transition state in the Cope and Claisen rearrangements of acyclic 1,5-dienyl systems is well-documented.[1,2] It has been demonstrated that a significant amount of product can arise from a boatlike transition state, particularly when one or both of the olefins are contained in a ring.[3] We present herein evidence that the Claisen rearrangement serves to trap the kinetically formed Cope rearrangement product during the tandem Cope–Claisen rearrangement.[4]

Thermolysis (377 °C, evacuated tube, 1.5 min) of vinyl ether **1b**, prepared by the method previously described,[4a] provided a 70:30 mixture of **4/5**. The diastereomeric ratio was found to be temperature dependent (306 °C, 0.5 h, 77:23; 257 °C, 5.6 h, 81:19) in contrast to the lack of selectivity and absence of temperature dependence in the rearrangement **1b** → **4, 5** (secondary methyl = hydrogen).[4a] The 270-MHz ^{1}H NMR spectrum of the major component **4** revealed characteristic resonances at δ 9.67 (t, J = 3 Hz, CHO), 1.08 (s, R_3CCH_3), and 1.07 (d, J = 7 Hz, R_2CHCH_3) while the minor component **5** displayed resonances at δ 9.72 (t, J = 3 Hz, CHO), 1.31 (s, R_3CCH_3), and 1.10 (d, J = 7 Hz, R_2CHCH_3).

The stereochemistry of **4** was established by transformation (Scheme I) of a mixture of **4/5** (85:15) into a mixture of diketones **8/9** (80:20). The major diketone was found to be identical (270-MHz NMR) with a sample prepared from ketone **10**, which has been previously converted to damsinic acid **11**.[5,6]

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